CLAIMS

1. Porous hydrophilic membranes comprising a porous inert support on which an ionomer is deposited, said membranes being characterized in that they have an ionic conductivity in electrochemical cells and a water permeability higher than 1 $l/(h.m^2.Atm)$; the ionomer being under amorphous form and having the hydrophilic group in the acid form.

2. Membranes according to claim 1, having pores partially or totally occluded to gases.

3. Membranes having pores totally occluded to gases according to claims 1-2, containing an ionomer amount higher than about 30% by weight.

4. Membranes having pores partially occluded to gases according to claims 1-2, containing an ionomer amount lower than about 20% by weight.

5. Membranes according to claims 1-4, wherein the porous support is formed by (per)fluoropolymers, preferably PTFE, still more preferably bistretched PTFE.

6. Membranes according to claims 1-5, wherein the ionomers are (per)fluorinated polymers and they preferably have SO_3H and/or -COOH, preferably SO_3H, functionality, and an equiavalent weight such as to result amorphous.

7. Membranes according to claim 6, wherein the ionomers com-

prise:

(A) monomeric units deriving from one or more fluorinated monomers containing at least one ethylene unsaturation;

(B) fluorinated monomeric units containing functional groups transformable into hydrophilic groups preferably $-SO_2F$ and/or COOR, COF, wherein R is a C_1-C_{20} alkyl radical or a C_6-C_{20} aryl radical, in such an amount to give the above equivalent weight, the functional groups being converted into hydrophilic groups, preferably into $-SO_3H$ and/or -COOH groups in the final membrane if the functional groups were $-SO_2F$ and/or -COOR, -COF.

8. Membranes according to claim 7, wherein the fluorinated monomers of type (A) are selected from the following:

- vinylidene fluoride (VDF);
- C_2-C_8 perfluoroolefins, preferably tetrafluoroethylene (TFE);
- C_2-C_8 chloro- and/or bromo- and/or iodo-fluoroolefins, such as chlorotrifluoroethylene (CTFE) and bromotrifluoroethylene;
- $CF_2=CFOR_f$ (per)fluoroalkylvinylethers (PAVE), wherein R_f is a C_1-C_6 (per)fluoroalkyl, for example trifluoromethyl, bromodifluoromethyl, pentafluoropropyl;

- CF_2=CFOX perfluoro-oxyalkylvinylethers, wherein X is a C_1-C_{12} perfluoro-oxyalkyl having one or more ether groups, for example perfluoro-2-propoxy-propyl.

9. Membranes according to claims 7-8, wherein the fluorinated monomers of type (B) are selected from the following:

- F_2C=CF-O-CF_2-CF_2-SO_2F;
- F_2C=CF-O-[CF_2-CXF-O]$_n$-CF_2-CF_2-SO_2F

wherein X = Cl, F or CF_3; n = 1-10;

- F_2C=CF-O-CF_2-CF_2-CF_2-SO_2F
- F_2C=CF-Ar-SO_2F wherein Ar is an aryl ring;
- F_2C=CF-O-CF_2-CF_2-CF_2-COF
- F_2C=CF-O-[CF_2-CXF-O]$_n$-CF_2-CFX-COF

wherein X = Cl, F or CF_3; n = 1-10.

10. Membranes according to claims 1-9, wherein the ionomers contain from 0.01 to 5% by moles of monomeric units deriving from a bis-olefin of formula:

$$R_1R_2\ C = CH\ -(CF_2)_m-\ CH = CR_5R_6 \qquad (I)$$

wherein:

m = 2-10, preferably 4-8;

R_1, R_2, R_5, R_6, equal to or different from each other, are H or C_1-C_5 alkyl groups.

11. Membranes according to claims 1-10, wherein the ionomers comprise:

- monomeric units deriving from TFE;

- monomeric units deriving from $CF_2=CF-O-CF_2CF_2SO_2F$;
- monomeric units deriving from the bis-olefin of formula (I);
- iodine atoms in end position.

12. Membranes according to claims 1-11, wherein the amorphous ionomer shows a substantial absence of crystallinity.

13. Membranes according to claims 1-11, wherein the amorphous ionomer has a residual crystallinity lower than 5%, preferably lower than 1%.

14. Membranes according to claims 1-13, wherein the (per)fluorinated ionomers are crosslinked.

15. Membranes according to claims 1-13, containing one or more amorphous or crystalline (per)fluoropolymers, the amorphous ones being different from the ionomer used in the membrane.

16. Membranes according to claim 15, wherein the (per)fluoropolymers are of crystalline ionomeric type.

17. Use of the membranes according to claims 1-16 in electrochemical cells.

18. Use of the membranes according to claim 17 for fuel cells.

19. Use of the membranes according to claim 18, wherein in the fuel cells the membranes of claim 4 are used and an air pressure is used at the cathode side higher than that

of the hydrogen at the anode side, the fed hydrogen coming from reforming and therefore containing CO.

20. A process for preparing hydrophilic porous membranes according to claims 1-16, comprising a porous support formed by a (per)fluorinated polymer, and amorphous (per)fluorinated ionomers containing hydrophilic groups, preferably having a $-SO_3H$ or -COOH functionality, said process comprising the following steps:

a) impregnation of the porous support formed by the (per)fluorinated polymer, with a (per)fluorinated ionomer having hydrolyzable functions, preferably $-SO_2F$, -COOR, -COF, wherein R is a C_1-C_{20} alkyl radical or a C_6-C_{20} aryl radical, using a solution of the ionomeric compound in fluorinated organic solvent at a concentration in the range 1-20% by weight, preferably 4-20% by weight until obtaining a membrane having the pores substantially filled by the ionomeric solution, the impregnation is carried out at temperatures between the room temperature and 120°C, preferably between 15°C and 40°C; the so impregnated membrane is subjected to thermal treatment at temperatures from 50° to 200°C, preferably from 120° to 160°C until substantial removal of the solvent and obtainment of a substantially transparent

membrane, optionally step a) is repeated until the membrane appears substantially transparent;

b) treatment of the membrane obtained in a) with inorganic strong, preferably aqueous, alkales, i.e. bases which are completely dissociated in water, to obtain the conversion of the functional groups into hydrophilic groups, preferably from $-SO_2F$ into $-SO_3^-$, and of the -COOR, -COF groups into $-COO^-$ groups;

c) treatment of the membrane obtained in b) with inorganic strong acids, i.e. acids which are completely dissociated in aqueous solution, obtaining the (per)fluorinated ionomer in acid hydrophilic form;

d) optionally treatment with water at temperatures in the range 50°C-100°C, in case repeated, until removal of the ionomer in excess and neutral pH of the washing waters.

21. A process according to claim 20, wherein in step a) the solvent has a boiling point at room pressure lower than 180°C, preferably lower than 120°C.

22. A process according to claims 20-21, wherein in step b) the used strong alkales are the hydroxides of the Group Ia metals.

23. A process according to claims 20-22, wherein at the end of step b) washings with water are carried out until a

neutral pH of the washing waters is obtained.

24. A process according to claims 20-23, wherein the ionomer is crosslinked by adding to the impregnation solution a) crosslinking agents.

25. A process according to claim 24, wherein crosslinking takes place by adding peroxides to the impregnation solution and operating at temperatures from 100 to 300°C.